Radioactivity, Radionuclides & Radiation
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Presentation on Neutron Activation Analysis

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Outline

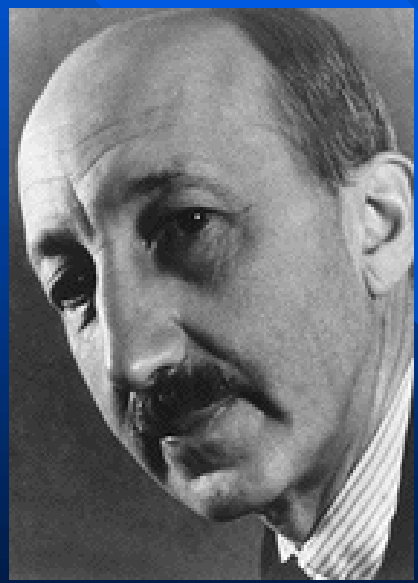
- Introduction to Neutron Activation Analysis
- Using Nuclides.net to solve simple activation problems
- NAAPRO – a versatile tool for predicting performance of NAA

Basics of Neutron Activation Analysis

- NAA is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor, and trace elements in samples from almost every conceivable field of scientific or technical interest.
- NAA offers sensitivities that are superior to those attainable by other methods, on the order of parts per billion or better.
- Because of its accuracy and reliability, NAA is generally recognized as the "referee method" of choice.
- It is estimated that approximately 100,000 samples undergo NAA analysis each year.

Pioneers of Neutron Activation Analysis

- Neutron activation analysis was discovered in 1936 when Hevesy and Levi found that samples containing certain rare earth elements became highly radioactive after exposure to a source of neutrons.



George de Hevesy: 1885 - 1966.
The Nobel Prize in Chemistry 1943.

Hilde Levi: 1909 - 2003

The NAA method

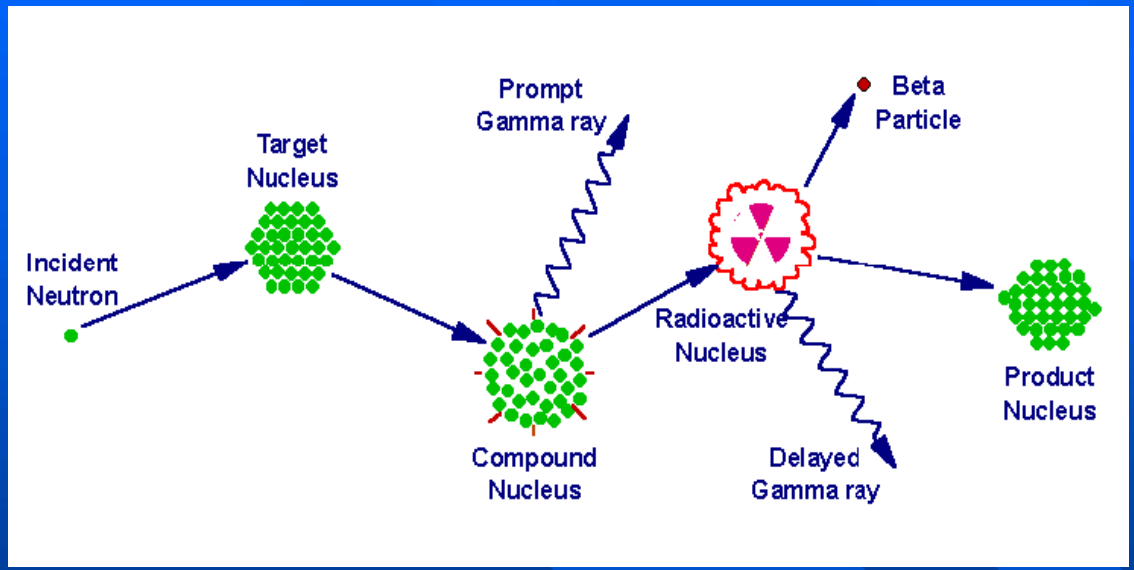


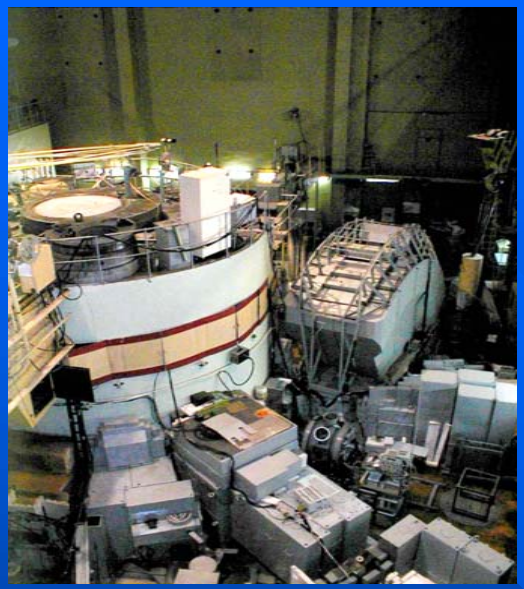
Diagram illustrating the process of neutron capture by a target nucleus followed by the emission of gamma rays.

Pictures taken from Michael D. Glascock
University of Missouri Research Reactor (MURR)

With respect to the time of measurement, NAA falls into two categories:

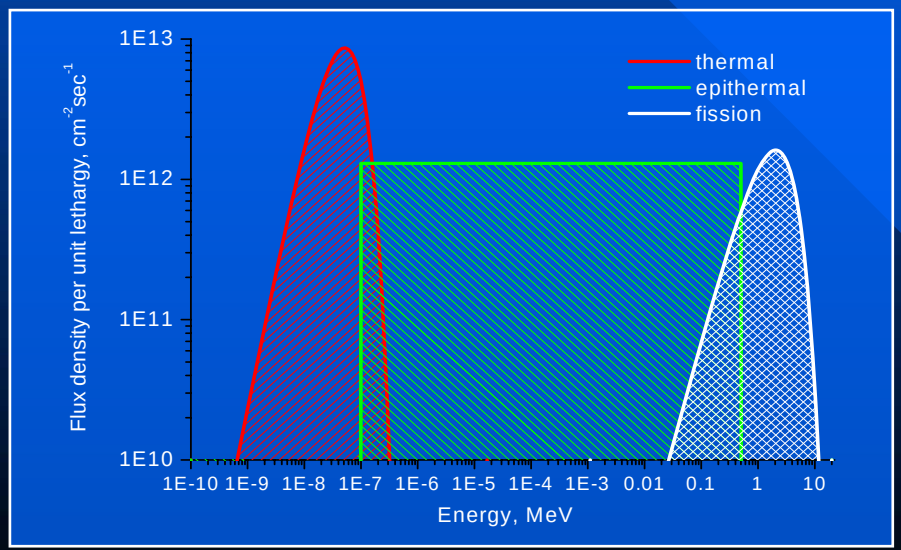
- prompt gamma-ray neutron activation analysis (PGNAA), where measurements take place during irradiation, or
- delayed gamma-ray neutron activation analysis (DGNAA), where the measurements follow radioactive decay.

Reactor neutrons



10 MW water-water nuclear research reactor

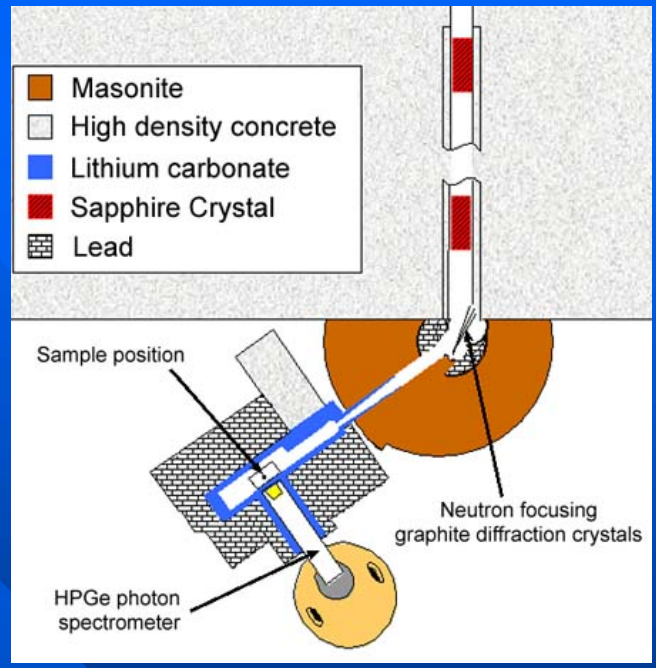
- **Thermal neutrons**: $E_n \leq 0.5$ eV. At room temperature, the energy spectrum of thermal neutrons is best described by a Maxwell-Boltzmann distribution with a mean energy of 0.025 eV and a most probable velocity of 2200 m/s.
- **Epithermal neutrons**: 0.5 eV < $E_n \leq 0.5$ MeV. A Cd foil 1 mm thick absorbs all thermal neutrons but will allow epithermal and fast neutrons above 0.5 eV in energy to pass through. Typically the epithermal neutron flux represents about 2% of the total reactor neutron flux. **ENAA** – Epithermal Neutron Activation Analysis.



- **Fast (fission) neutrons**: $E_n > 0.5$ MeV. Induce nuclear reactions where the ejection of one or more nuclear particles - (n,p), (n,n'), and (n,2n) - are prevalent. Typically about 5% of the total reactor neutron flux consists of fast neutrons. **FNAA** – Fast Neutron Activation Analysis.

Prompt NAA

PGNAA facility at MIT



The **PGNAA** technique is generally performed by using a beam of neutrons extracted through a reactor beam port.

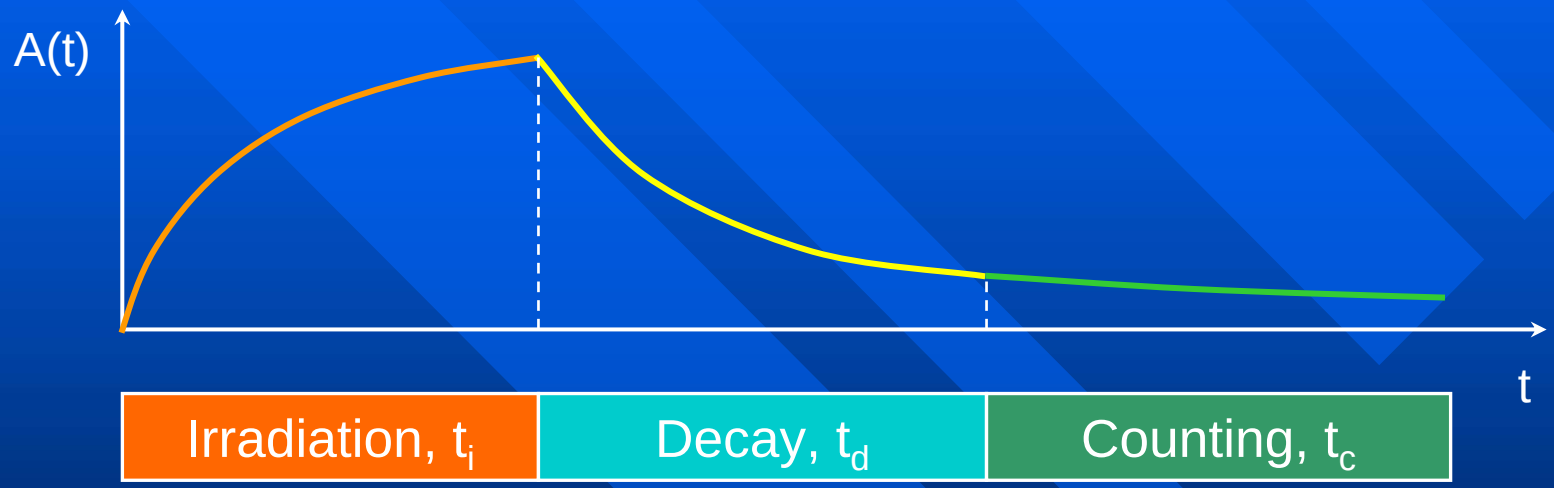
Utilization of the cold neutrons and chopped beams is more preferable for the better background conditions and highest sensitivity of the analysis.

The **PGNAA** technique is most applicable to elements:

- with extremely high neutron capture cross-sections (B, Cd, Sm, and Gd);
- elements which decay too rapidly to be measured by DGNAA;
- elements that produce only stable isotopes;
- elements with weak decay gamma-ray intensities.

Delayed NAA (conventional NAA)

- The **DGNAA** technique is useful for the vast majority of elements that produce radioactive nuclides. It consists of the tree principal steps:



- DGNAA is flexible with respect to time such that the sensitivity for a long-lived radionuclide that suffers from an interference by a shorter-lived radionuclide can be improved by waiting for the short-lived radionuclide to decay. This selectivity is a key advantage of DGNAA over other analytical methods.

Radiochemical vs. Instrumental NAA

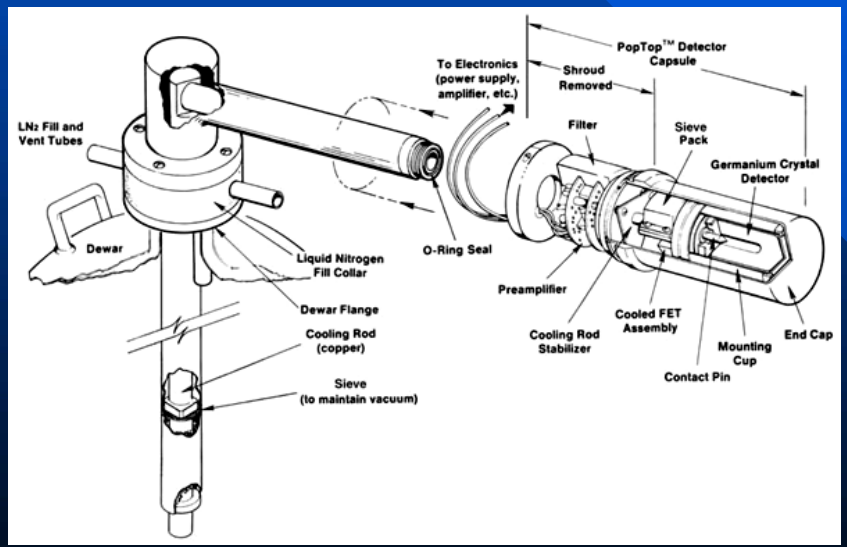
- The application of purely instrumental procedures is commonly called **Instrumental Neutron Activation Analysis** (**INAA**) and is one of NAA's most important advantages over other analytical techniques.

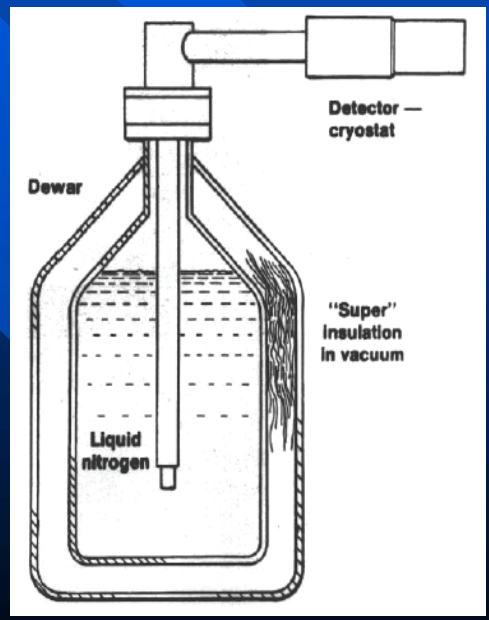
- If chemical separations are done to samples after irradiation to remove interferences or to concentrate the radioisotope of interest, the technique is called **Radiochemical Neutron Activation Analysis** (**RNAA**). This technique is performed infrequently due to its high labor cost.

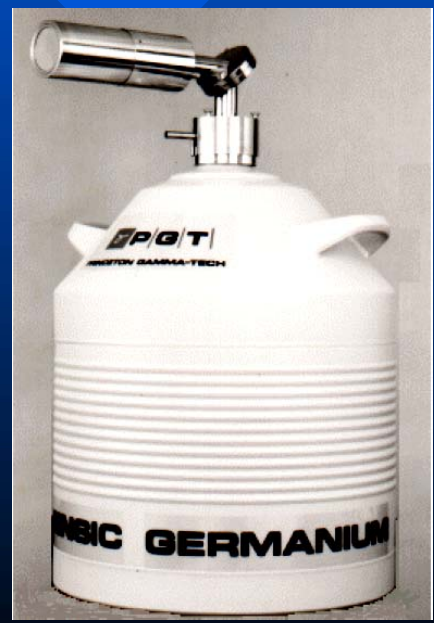
Ion exchange is a commonly used technique for post-irradiation sample treatment in RNAA

Measurement of Gamma Rays

- The instrumentation used to measure gamma rays from radioactive samples generally consists of a semiconductor detector, associated electronics, and a computer-based multi-channel analyzer.
- Hyperpure or intrinsic germanium (**HPGe**) detectors are commonly used. These detectors operate at liquid nitrogen temperatures (77 degrees K) by mounting the germanium crystal in a vacuum cryostat, thermally connected to a copper rod or "cold finger".

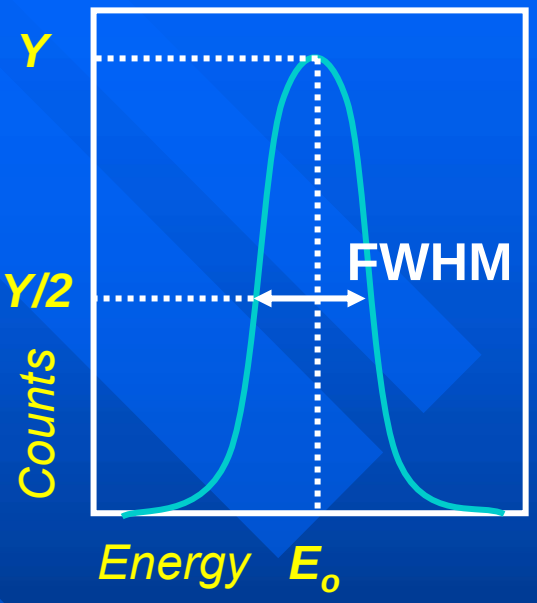






Important detector performance characteristics

- **Detector Resolution** is a measure of its ability to separate closely spaced Full Energy Peaks (**FEP**) in a spectrum. Detector resolution is specified in terms of the full width at half maximum (**FWHM**) of the 122-keV peak of Co-57 and the 1332-keV peak of Co-60.



- **Full Energy Peak Efficiency** is a measure of a detector ability to completely absorb the energy of a gamma ray.

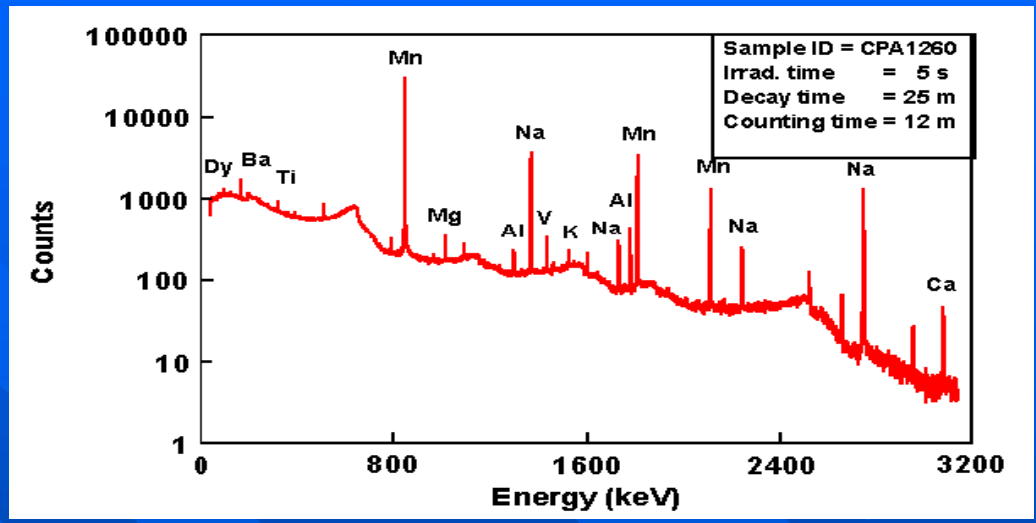
$$\text{FEP Efficiency} = \frac{\text{Number of counts in FEP}}{\text{Number of gamma rays emitted by a source}}$$

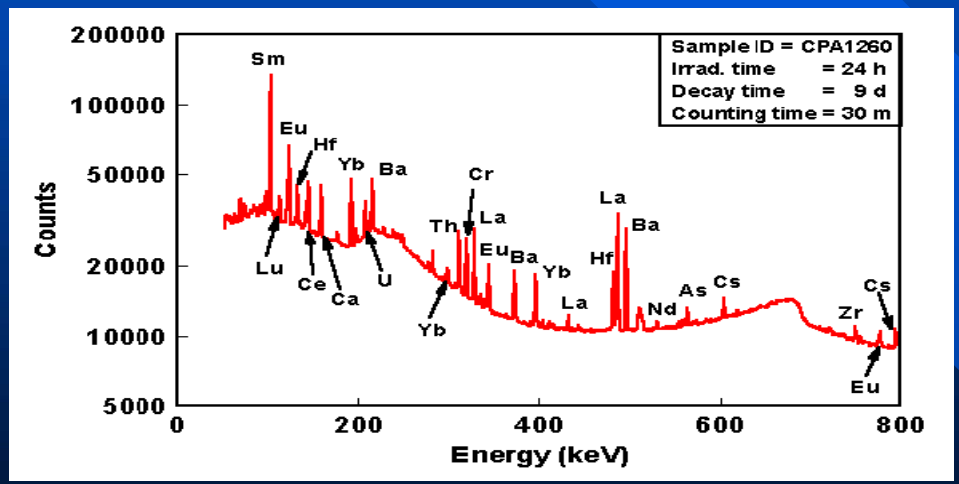
It is usually expressed in % relative to the value of $1.2 \cdot 10^{-3}$, which represents the efficiency of a 3-inch by 3-inch sodium iodide (**NaI**) detector for a Co-60 source (1332-keV gamma ray) at a distance of 25 cm from the crystal face.

Typical gamma-ray spectra

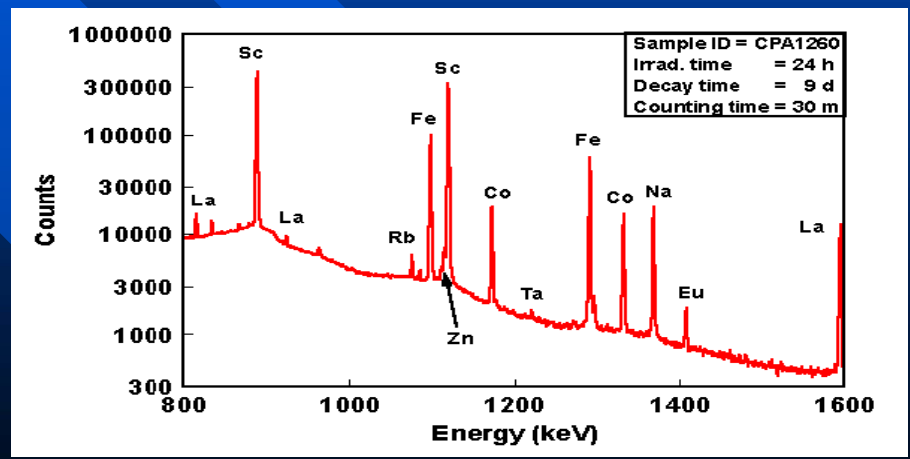
(on the example of an irradiated pottery specimen)

Short-term irradiation mode:
t_i = 5 s, t_d = 25 m, t_c = 12 m.



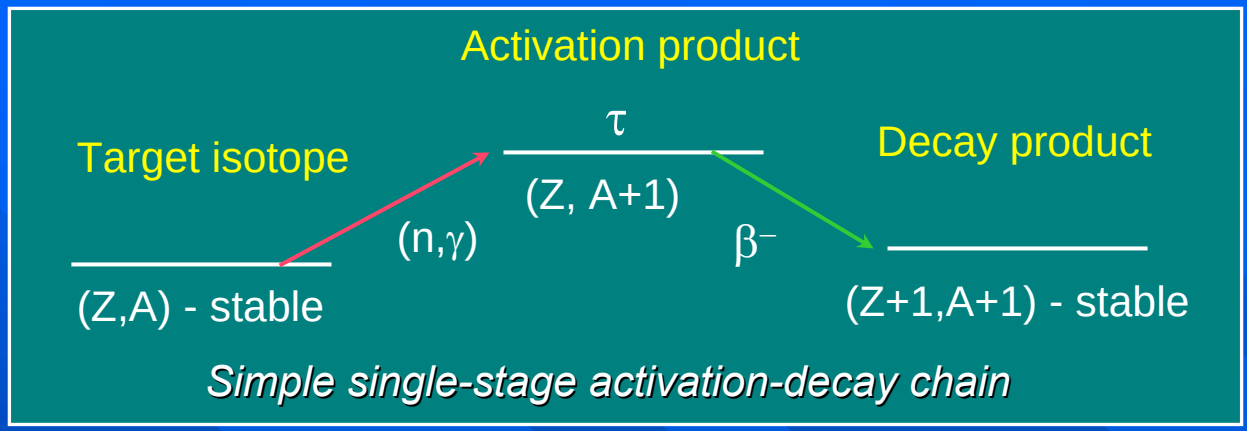


Long-term irradiation mode:
t_i = 24 h, t_d = 9 d, t_c = 30 m.



Pictures taken from Michael D. Glascock
University of Missouri Research Reactor (MURR)

FEP Counts



FEP number of counts: $S = A_{sat}\, C_i\, C_d\, C_c\, \gamma\, \varepsilon(E_\gamma)\, t_c$

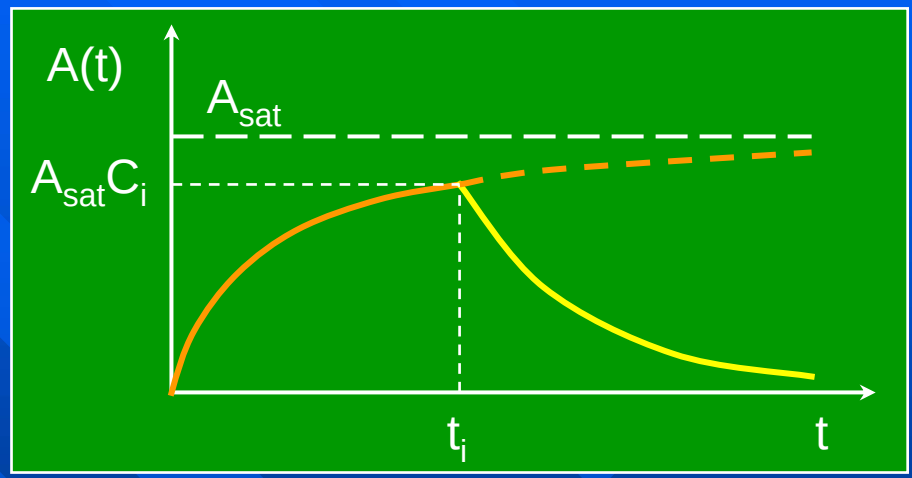
- A_{sat} – saturation activity;
- $C_i = 1-\exp(-\lambda t_i)$, $C_d = \exp(-\lambda t_d)$ and $C_c = (1-\exp(-\lambda t_c))/\lambda t_c$ – corrections for a decay of an activation product during irradiation, decay and counting time intervals respectively;
- γ – gamma ray emission probability;
- $\varepsilon(E_\gamma)$ – FEP efficiency for energy E_γ;
- t_i, t_d and t_c – irradiation, decay and counting time intervals respectively.

Calculating Element Concentration

$$A_{sat} = \frac{m\, f\, \rho\, N_A\, J}{M}$$

- m – sample mass, g;
- f – mass fraction of an element, g/g;
- ρ – abundance of a target isotope;
- N_A – Avogadro's number, $mole^{-1}$;
- J – neutron capture reaction rate, s^{-1};
- M – atomic mass of an element, g/mole.

Illustration for the saturation activity



The procedure generally used to calculate concentration in the unknown sample is to irradiate the unknown sample and a comparator standard containing a known amount of the element of interest together in the reactor. The equation used to calculate the mass of an element in the unknown sample relative to the comparator standard is

$$f_x = f_{std} \frac{A_{sat}^{x}}{A_{sat}^{std}}$$

Simple Activation Problem: formulation

- **Problem**: A 200 mg soil sample is irradiated in a reactor for 5 min. Consider activation of Al, whose mass fraction in the sample is 4.7%. Calculate the saturation activity of an activation product, as well as its activity at the end of irradiation and on 30 min after the irradiation. Irradiating neutron flux: thermal neutrons – $\Phi_{th} = 5 \cdot 10^{10}$ cm^{-2}s^{-1}, epithermal neutrons – $\Phi_{epi} = 7 \cdot 10^{8}$ cm^{-2}s^{-1}. Effective temperature of the thermal neutron flux $T_{eff} = 300$ K.

$$A_{sat} = \frac{m\, f\, \rho\, N_A\, J}{M}$$

$$J = \Phi_{th} \cdot \sqrt{\frac{293.6}{T_{eff}}} \cdot \frac{\sqrt{\pi}}{2} \cdot \sigma_0(2200\,\mathrm{m/s}) + \Phi_{epi} \cdot I$$

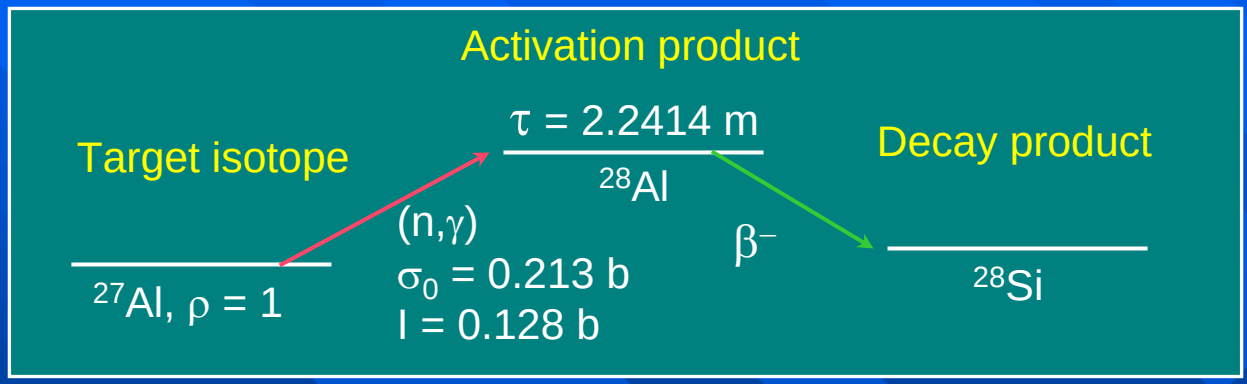
$$A(t_i) = A_{sat} \cdot C_i = A_{sat} \cdot (1 - \exp(-\lambda t_i))$$

$$A(t_i + t_d) = A(t_i) \cdot C_d = A(t_i) \cdot \exp(-\lambda t_d)$$

$$\lambda = \frac{\ln 2}{\tau}$$

Simple Activation Problem: solution

- Step #1: Using Nuclides Chart and DataSheet determine target isotope and its abundance, activation product and its half-live, decay product. Using X-section find cross-section at 2200 m/s and resonance integral for the neutron capture reaction on the target isotope.



- Step #2: Calculate reaction rate:

$$J = 5 \cdot 10^{10} \cdot \sqrt{\frac{293.6}{300}} \cdot \frac{\sqrt{\pi}}{2} \cdot 0.213 \cdot 10^{-24} + 7 \cdot 10^{8} \cdot 0.128 \cdot 10^{-24} = 0.9427 \cdot 10^{-14}\ s^{-1}$$

- Step #3: Calculate activities:

$$A_{sat} = \frac{0.2 \cdot 0.047 \cdot 1.0 \cdot 6.02 \cdot 10^{23} \cdot 0.9427 \cdot 10^{-14}}{26.982} = 1.977\ MBq$$

$$A(5\ m) = 1.977 \cdot (1 - \exp(-\frac{0.693 \cdot 5}{2.2414})) = 1.556\ MBq$$

$$A(35\ m) = 1.556 \cdot \exp(-\frac{0.693 \cdot 30}{2.2414}) = 145.8\ Bq$$

NAAPRO – a program for Neutron Activation Analysis PRognosis and Optimization

MARC-VI – Methods and Applications of Radioanalytical Chemistry, Kailua Kona, USA, April 2003
MTAA-11 – Modern Trends in Activation Analysis, Guildford, UK, June 2004

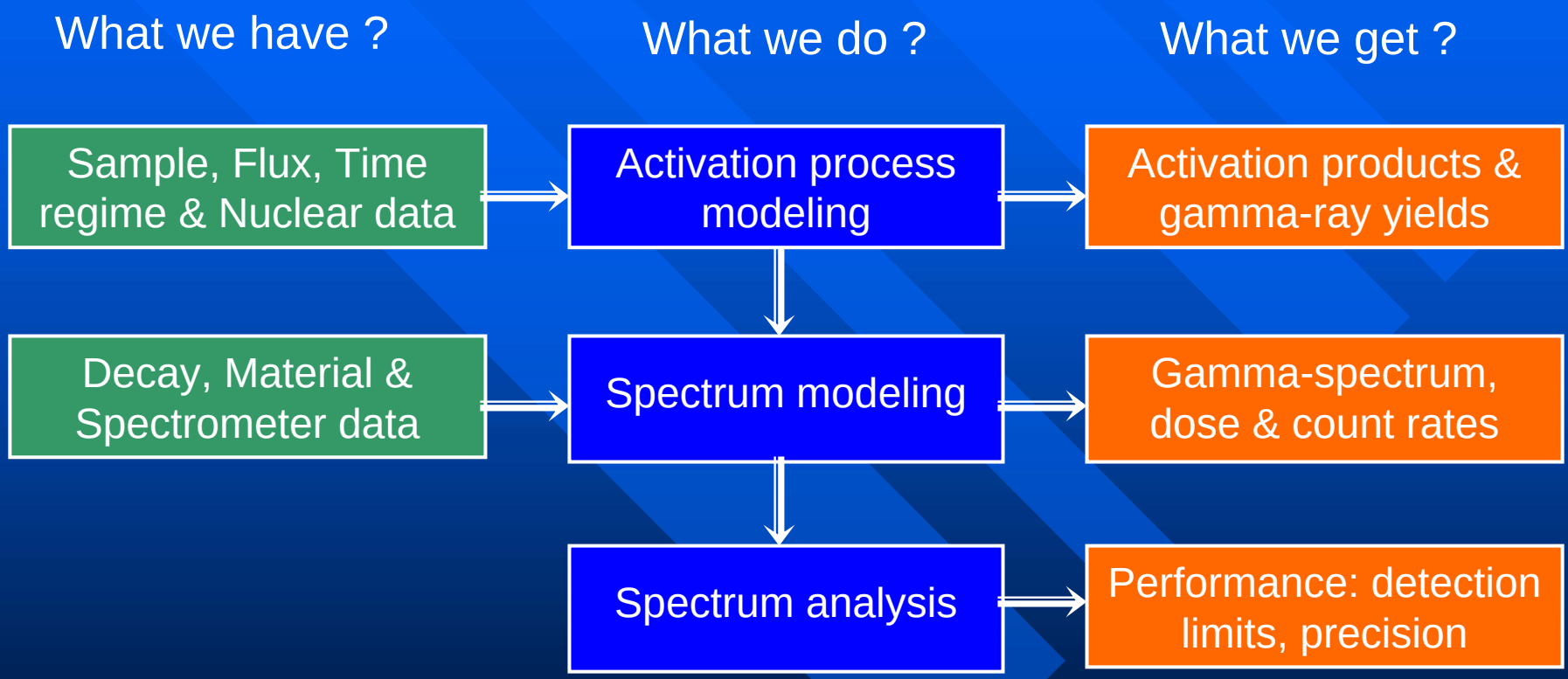
V.K. Basenko, A.N. Berlizov, I.A. Malyuk, V.V. Tryshyn, NAAPRO: A Code for Predicting Results and Performance of Neutron Activation Analysis, JRNC, Vol.263, No.3 (2005) pp. 675-681.

A.N. Berlizov, V.K. Basenko, R.H. Filby, I.A. Malyuk, V.V. Tryshyn, NAAPRO Detector Model, a Versatile and Efficient Approach to Gamma-Ray Spectrum Simulation, NIM A, 562 (2006) pp. 245-253.

V.K. Basenko, A.N. Berlizov, R.H. Filby, I.A. Malyuk, V.V. Tryshyn, Current Status and Prospects of Development of the NAAPRO Code, JRNC, Vol. 271, No. 2, 2007 (in press)

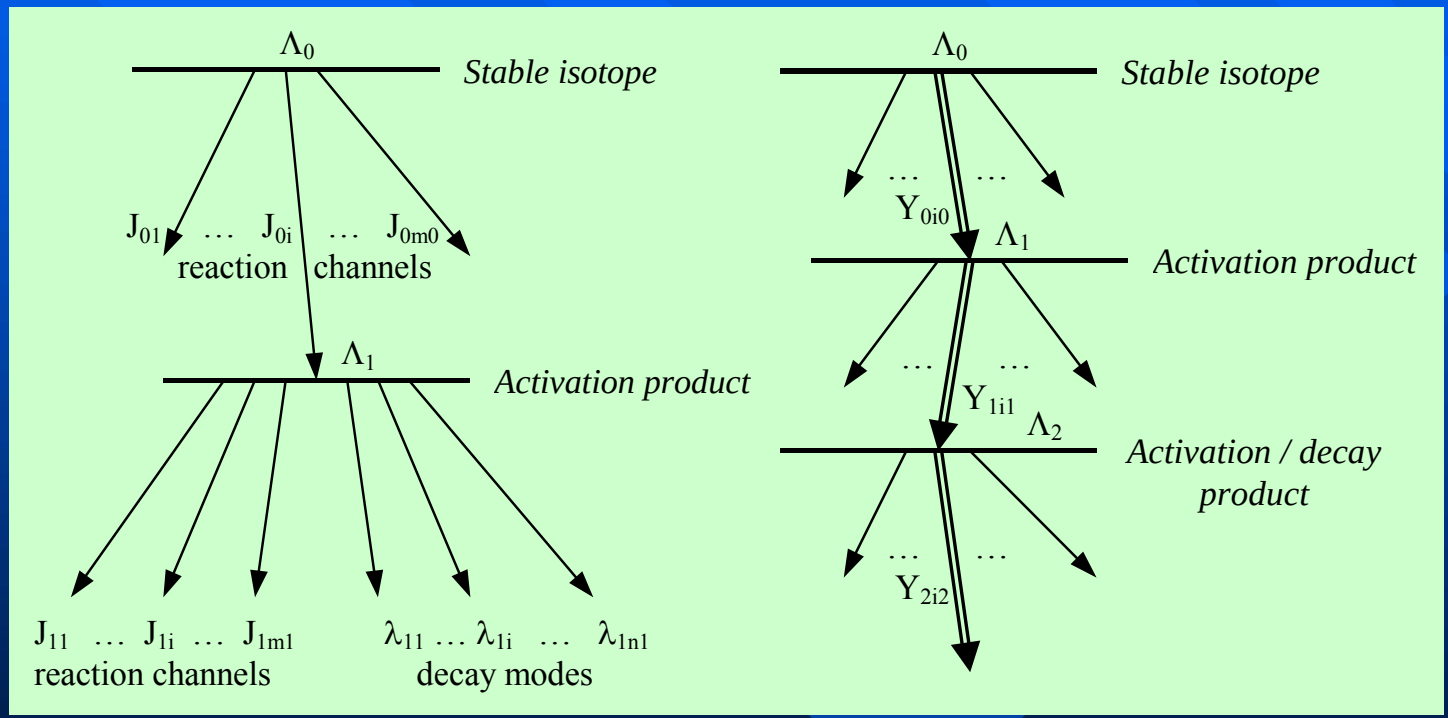
July 2004 – a Version 01.beta became available through RSICC (ORNL, http://www-rsicc.ornl.gov/) and OECD/NEA databank (Paris, http://www.nea.fr/html/dbprog/)

NAAPRO approach



Activation process modeling

A general case of activation of stable isotopes of a chemical element was considered. A Caushy problem for generalized nuclear transformation tree has been solved.



(a) – nuclear transformation tree at activation, (b) – selected nuclear transformation chain $c = \{i_0, i_1, \ldots, i_{Nc-1}\}$. Λ_i and Y_{ij} are generalized decay constant and branching coefficient respectively.

Activation process modeling: expressions

The probability of creation of the *i*-th radionuclide per nucleus of the element under the neutron exposure during irradiation time interval t_1 and its decay within the measurement time interval t_3 following cooling period t_2:

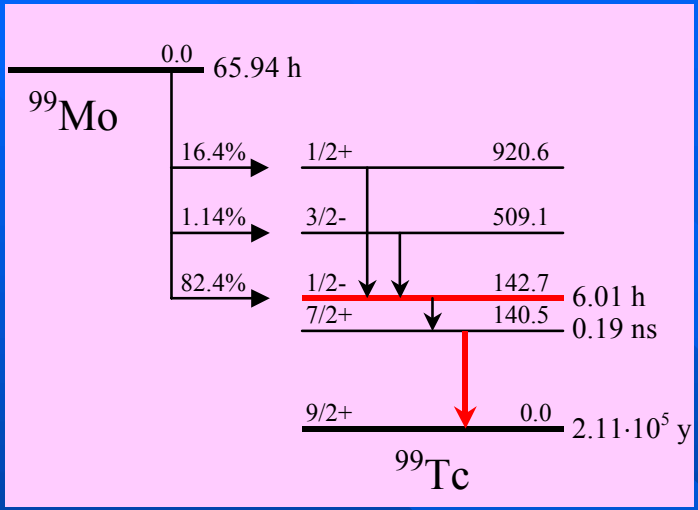
$$P_i = \sum_{n=1}^{N_{st}} \rho_n p_i^n = \sum_{n=1}^{N_{st}} \rho_n \sum_c p_{ic}^n$$

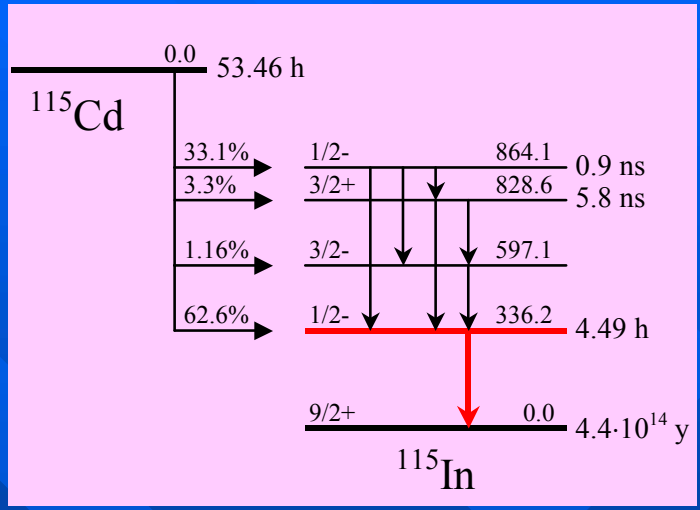
N_{st} – number of stable isotopes of the element considered, ρ_n – abundance of *n*-th stable isotope; p^n_{ic} – probability reduced per nucleus of the *n*-th stable isotope and per activation chain '*c*':

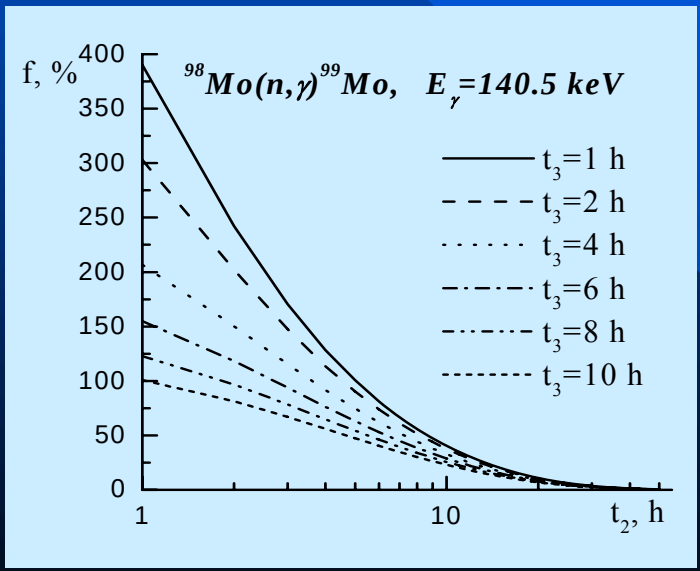
$$p_{ic}^n = \lambda_i^n \left(\prod_{k=0}^{i-1} \Lambda_k^n Y_{kc_k}^n \right) \sum_{j=N}^{i} \frac{exp(-\lambda_j^n t_2)}{\lambda_j^n} \left(1 - exp(-\lambda_j^n t_3)\right) \sum_{m=N}^{j} \frac{D_m^{-1}}{\prod_{\substack{k=m \\ k \neq j}}^{i} (\lambda_k^n - \lambda_j^n)} \sum_{l=0}^{m} \frac{exp(-\Lambda_l^n t_1)}{\prod_{\substack{k=0 \\ k \neq l}}^{m} (\Lambda_k^n - \Lambda_l^n)}$$

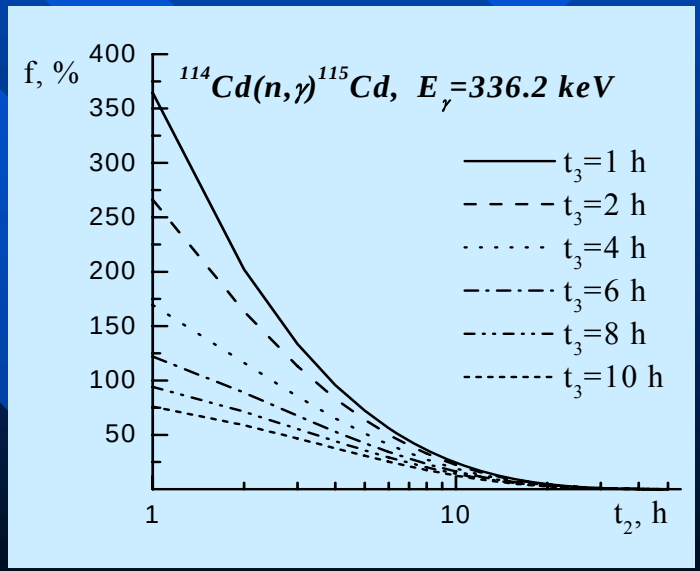
D_m – decontamination factors (RNAA).

Activation process modeling: example #1



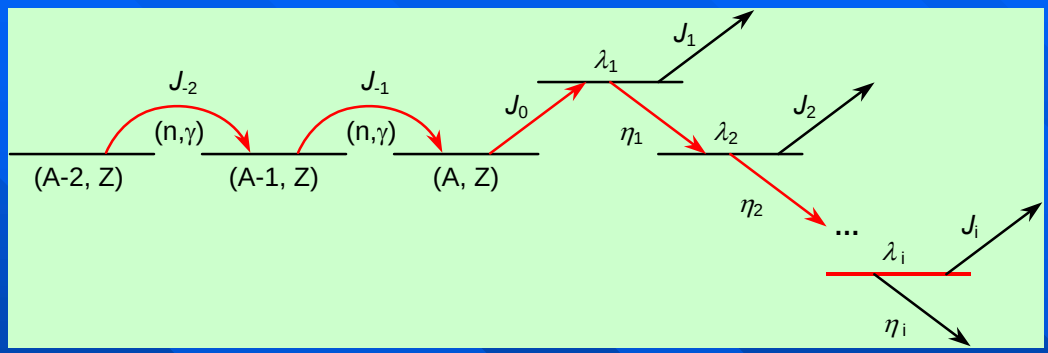






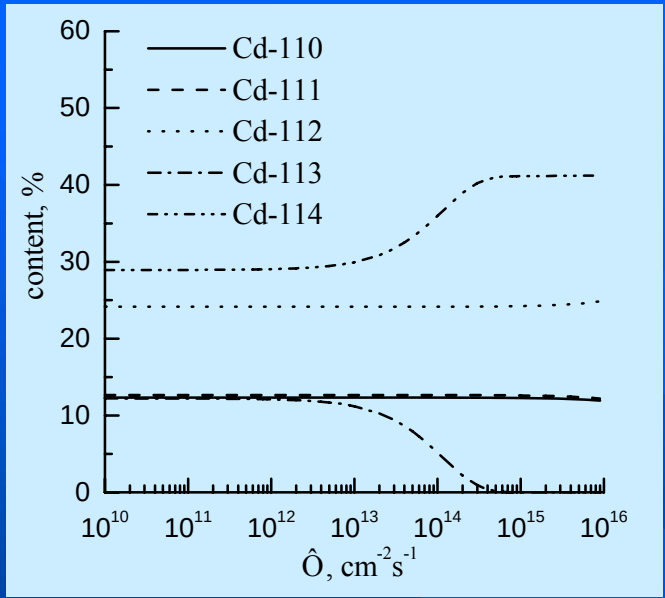
Activation process modeling: example #2

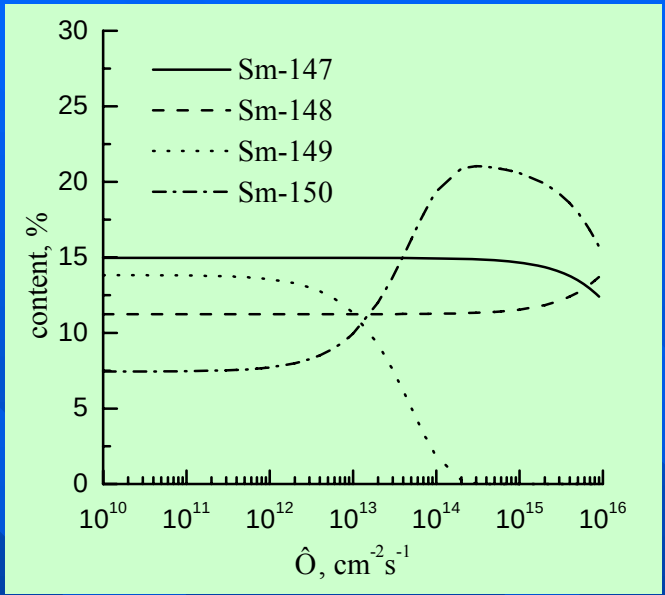
Burnup of stable isotopes:

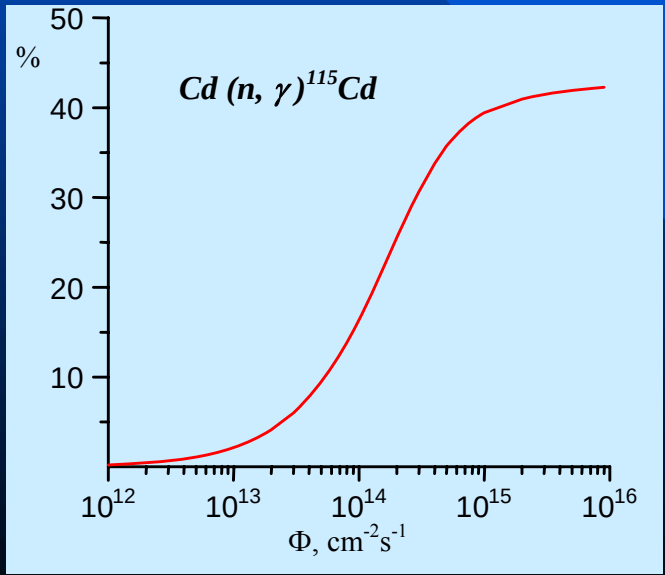


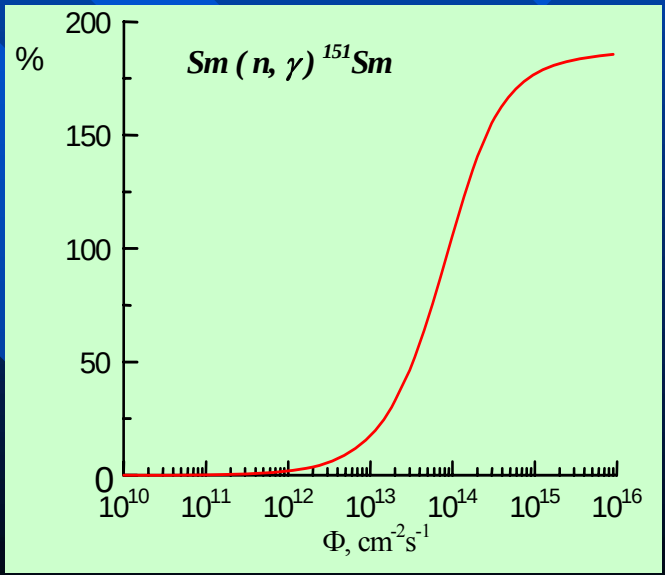
Isotope	*Content,%*	*Reaction*	*Product*	*$T_{1/2}$, day*	*σ, barn*
Cd-110	*12.32*	*(n,γ)*	*Cd-111*	*stable*	*10.0*
Cd-111	*12.67*	*(n,γ)*	*Cd-112*	*stable*	*21.7*
Cd-112	*24.15*	*(n,γ)*	*Cd-113*	*stable*	*2.1*
Cd-113	*12.21*	*(n,γ)*	*Cd-114*	*stable*	**23977.3**
Cd-114	*28.93*	*(n,γ)*	*Cd-115*	*2.2275*	*0.51*
Sm-147	*14.97*	*(n,γ)*	*Sm-148*	*stable*	*58.1*
Sm-148	*11.24*	*(n,γ)*	*Sm-149*	*stable*	*2.4*
Sm-149	*13.83*	*(n,γ)*	*Sm-150*	*stable*	**55887**
Sm-150	*7.44*	*(n,γ)*	*Sm-151*	*32850*	*95.7*

Activation process modeling: example #2









NAAPRO Nuclear Data Library

- Radionuclide library is based on the Evaluated Nuclear Structure Data File, appended by the KX- and LX-ray data and 511 keV photon intensities.
- Photon interaction data are taken from EPDL data library.
- Continuous and fixed (14 MeV) energy neutron cross-section libraries were built using the following data sources, arranged according to the assigned priorities:

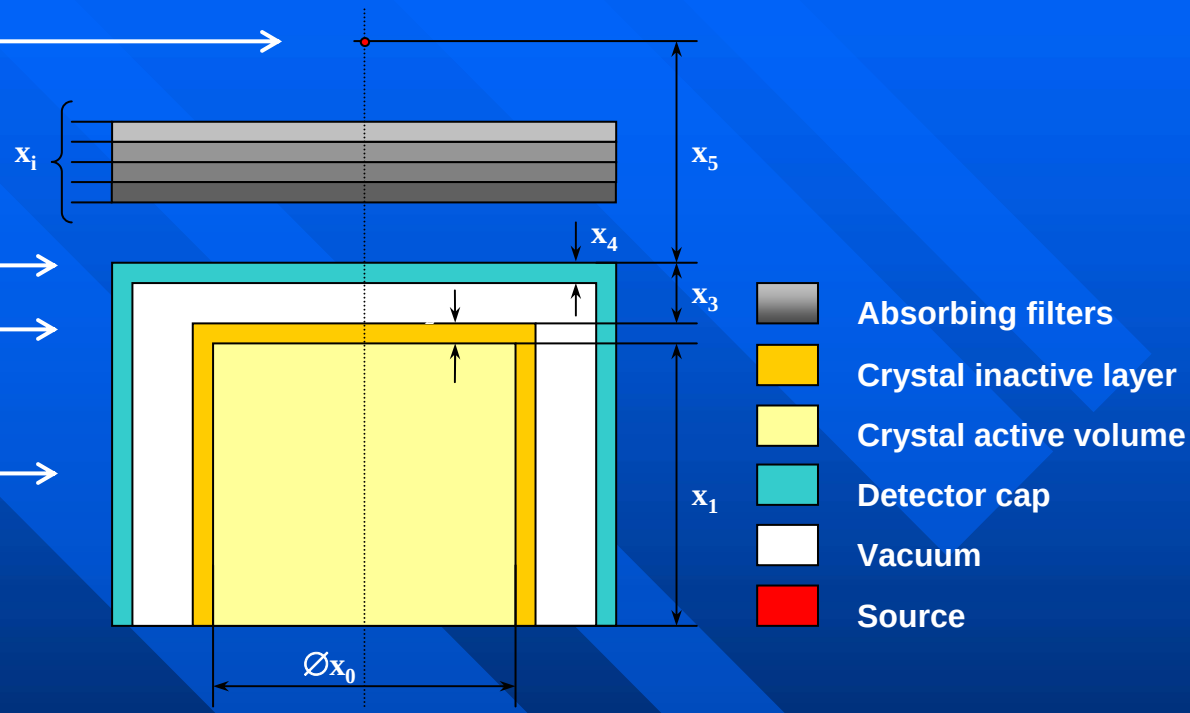
Data Library	Origin
EAF-4 – European Activation File	Energy research Center of the Netherlands, Petten, 1995
RNAL – Reference Neutron Activation Library	Nuclear Data Section, International Atomic Energy Agency, 2000
ENDF/B-VI Release 8 – Evaluated Nuclear Data File	Brookheaven National Laboratory, National Nuclear Data Center, USA, 2001
JENDL-3.2 – Japanese Evaluated Nuclear Data Library	Nuclear Data Center of Japan Atomic Energy Research Institute and Japanese Nuclear Data Committee, Japan, 1994
JEF-2.2 - Joint Evaluated File	European Library, NEA, 1992
BROND-2 –Russian Evaluated Neutron Reaction Data Library	Institute of Physics and Power Engineering, Obninsk, Russian Federation, 1994
CENDL-2 – Chinese Evaluated Nuclear Data Library	Chinese Nuclear Data Center, Institute of Atomic Energy, China, 1995
ADL-3 – Activation Data Library	Institute of Physics and Power Engineering, Obninsk, Russian Federation, 1994

Spectrum modeling: detector model

Arbitrary source to detector distance

Up to 10 absorbing layers in addition to the detector input window and inactive layer of the crystal.

Arbitrary crystal material: Ge, NaI, BGO; and dimensions:
x_0 & x_1 = [3 cm, 10 cm]
(4 – 250 % rel. eff. HPGe)



Detector response function:

$$G(E,E_i) = \varepsilon_{tot}(E_i) \cdot \{\omega_{FE}(E_i)\cdot g_p(E,E_i) + \omega_{SE}(E_i)\cdot g_P(E,E_i-m_0c^2) + \omega_{DE}(E_i)\cdot g_p(E,E_i-2m_0c^2) +$$

$$+ (1 - \omega_{FE}(E_i) - \omega_{SE}(E_i) - \omega_{DE}(E_i)) \cdot (g_C(E,E_i) + k_{BS}\cdot g_{BS}(E,E_i))\}$$

Spectrum modeling: detector efficiency

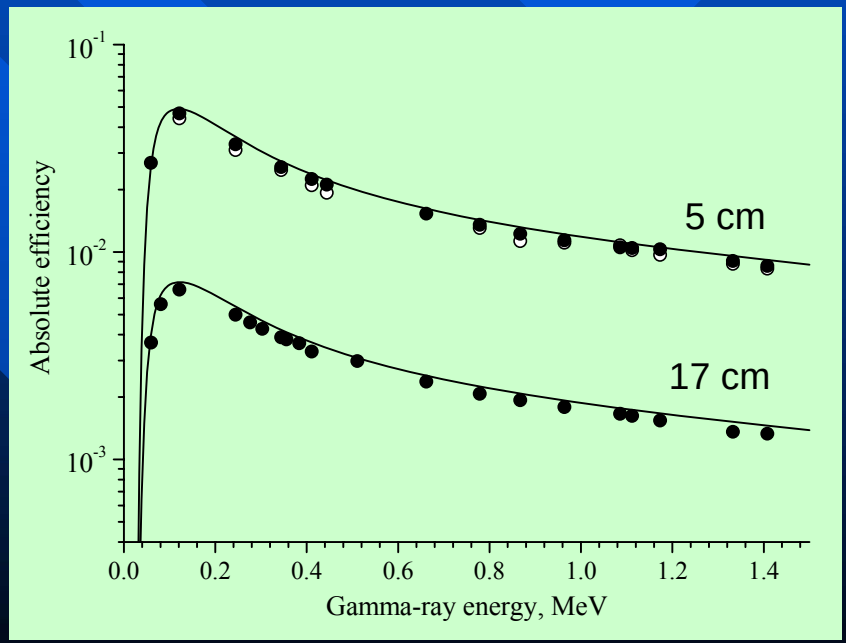
- Total efficiency - numerical integration over the detector sensitive volume:

$$\varepsilon_{tot} = \frac{1}{2}\left\{\int_{\eta_1}^{1}\left[1-\exp(-\mu_c H/t)\right]\cdot\exp(-\mu_a x_a/t)\cdot dt + \int_{\eta_2}^{\eta_1}\left[1-\exp(\mu_c L/t - \mu_c R/\sqrt{1-t^2})\right]\cdot\exp(-\mu_a x_a/t)\cdot dt\right\}$$

- Photofraction & SE and DE peak to total ratios – MCNP calculations for a bare crystal in the range 3 – 10 cm both for height and diameter with 1×1 cm^2 mesh, energy range from 5 keV to 4000 keV, and source to crystal distances – 0 cm, 4 cm, and 10 cm.

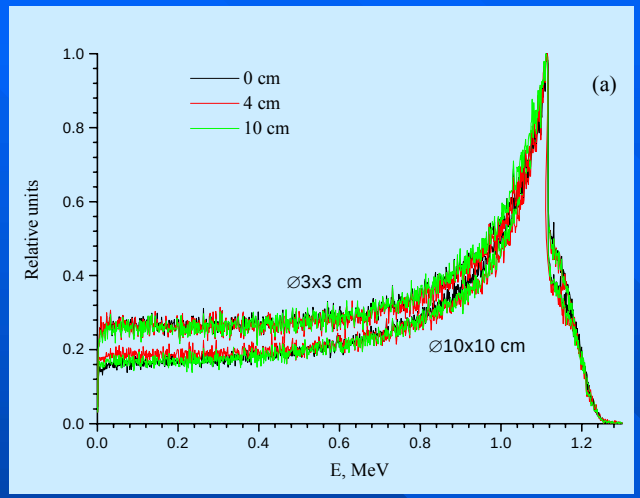
- Example:

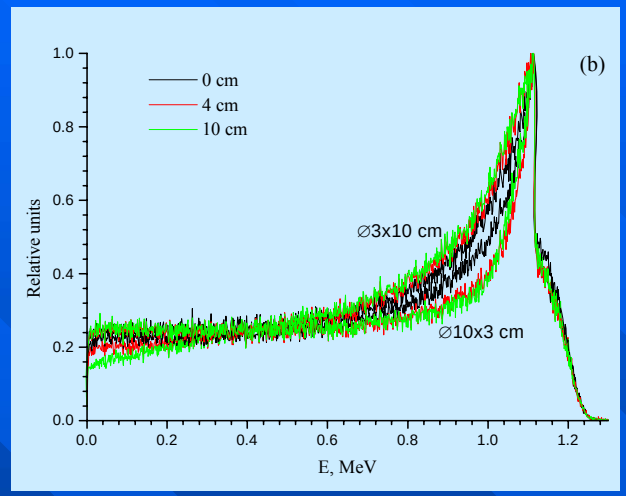
  detector – coaxial 60% HPGe;
  model – GC6020 (Canberra);
  crystal dimensions – ∅74×53 mm;
  inactive Ge – 0.07 cm;
  detector end cap – 0.15 cm Al;
  detector end cap to crystal – 0.5 cm.



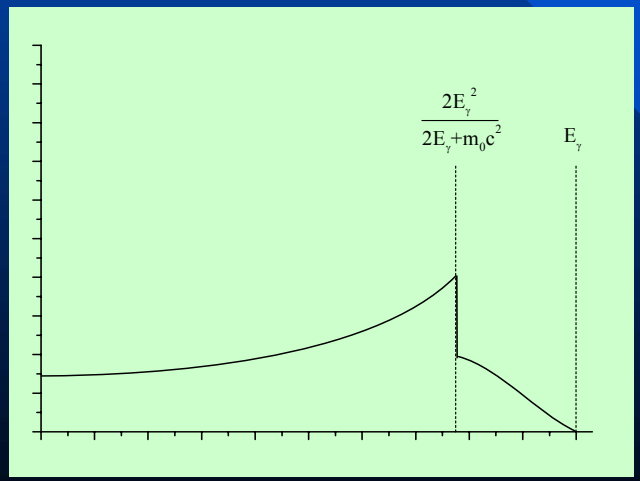
Spectrum modeling: Compton continuum

Testing Compton continuum shapes:

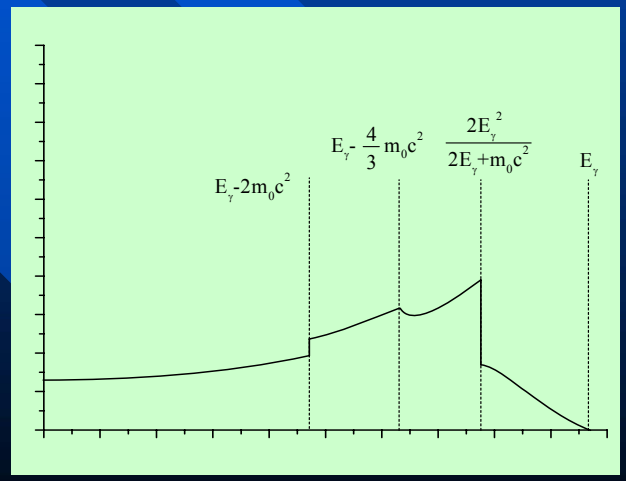




Regions of Compton continuum parameterization:



$E_\gamma \leq 1022$ keV



$E_\gamma > 1022$ keV

Spectrum modeling: g_{BS} & background

- Backscatter peak shape function:

$$g_{BS}(E',E) = \frac{1}{N}\int_{E_{min}}^{E} g_P(E',E'')\cdot\sigma_c(E-E'',E)\cdot\varepsilon_{FE}(E'')\cdot dE''$$

- Background radiation spectrum model:

B = B(continuum) + B(discrete)

$$B(\,continuum\,) \propto \int_{\Delta N} \varepsilon_{FE}(E)\frac{dE}{E}$$

$$B(\,discrete\,) \propto \sum_i \frac{I_i}{\varepsilon_{FE}(E_i)}\int_{\Delta N} g(E,E_i)dE$$

Spectrum modeling: real example

Facility: nuclear research reactor WWR-10M, INR, Kyiv, Ukraine.

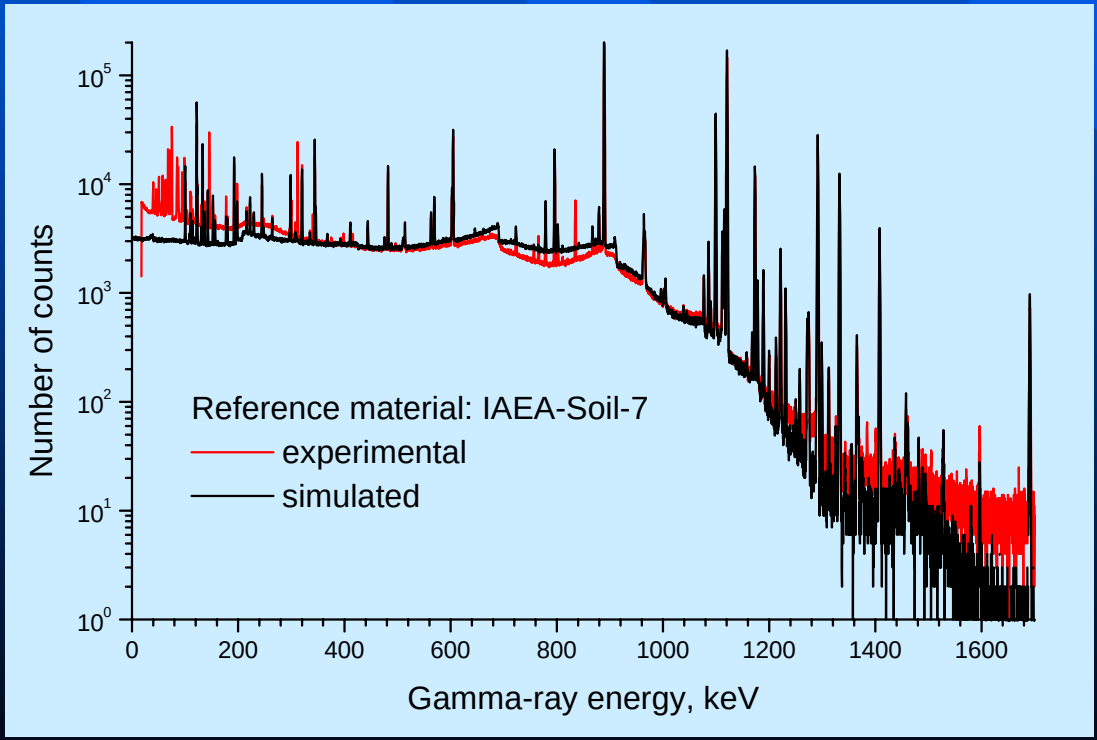
Reference material: soil - IAEA-Soil-7 (m=25 mg).

Irradiation modes: irradiation - 170 h, cooling – 59 days, measurement – 10000 s.

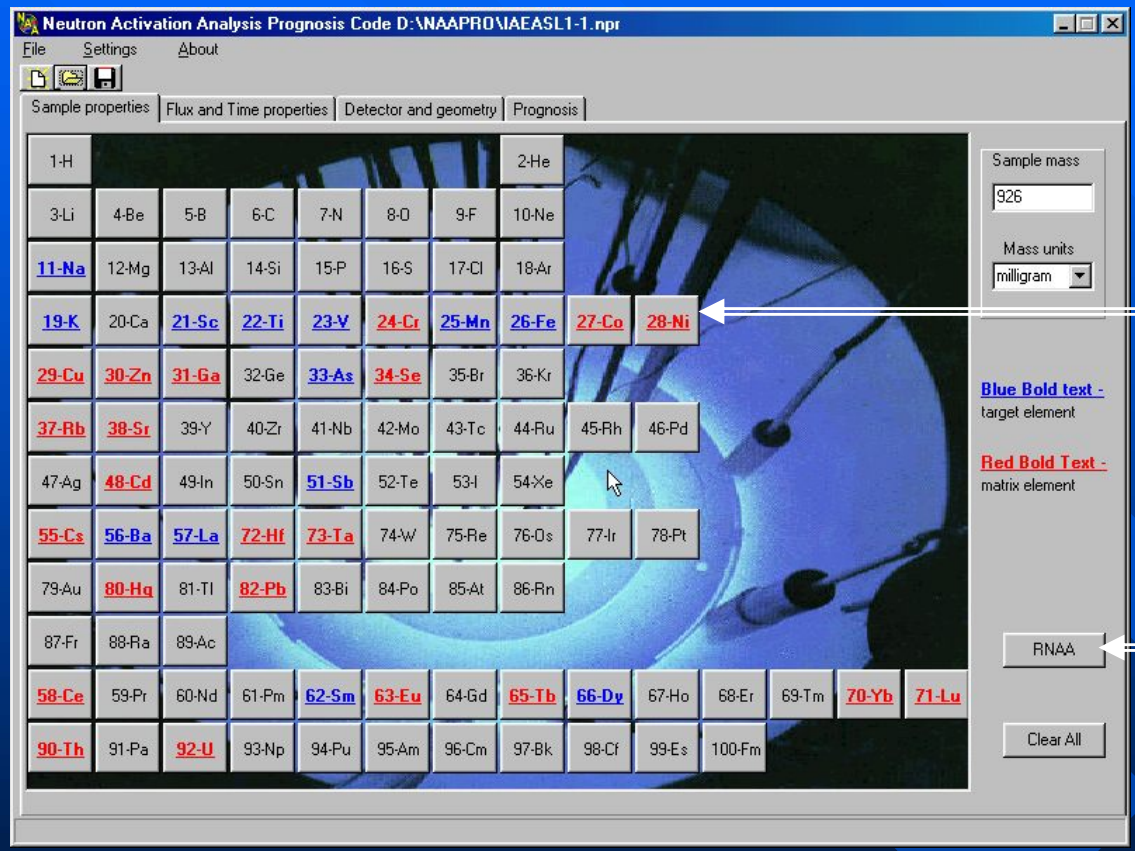
Neutrons: thermal - $1.7 \cdot 10^{13}$ $cm^{-2}s^{-1}$; epithermal - $1.3 \cdot 10^{12}$ $cm^{-2}s^{-1}$; fission - $3.4 \cdot 10^{12}$ $cm^{-2}s^{-1}$.

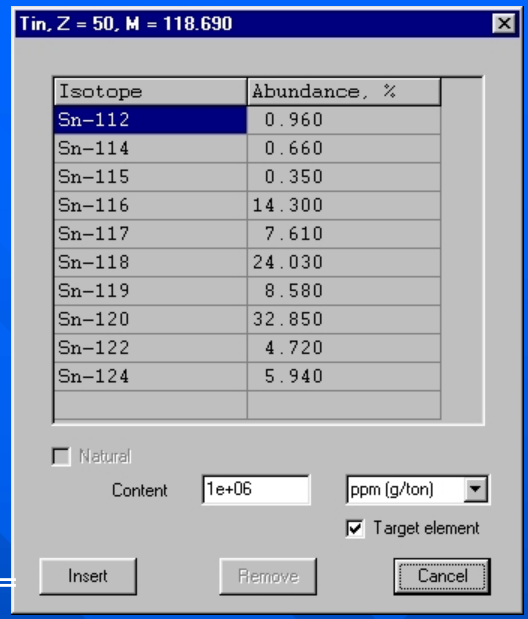
Detector: coaxial HPGe with 61.8% rel. eff., FWHM < 1.9 keV at 1332.5 keV ^{60}Co.

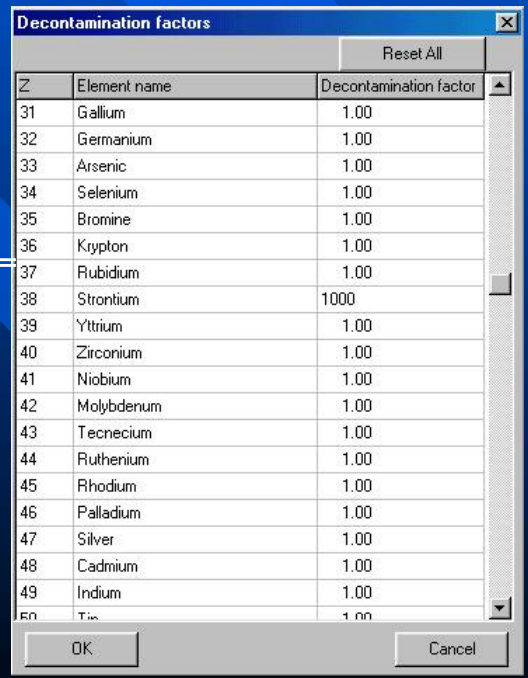
Electronics: DSP9660, LFC599, and AIM556 (Canberra).



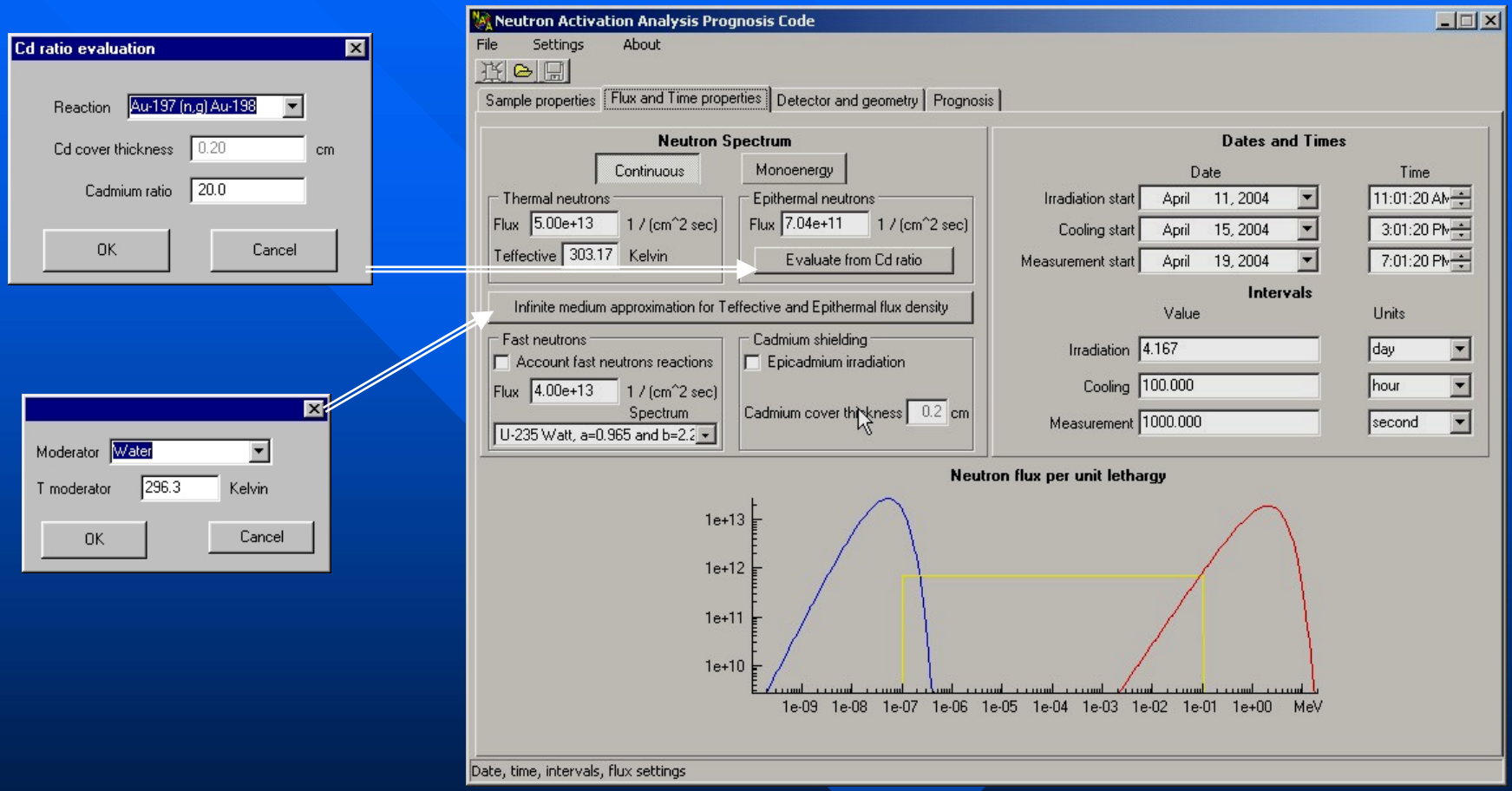
NAAPRO GUI: Sample properties tab



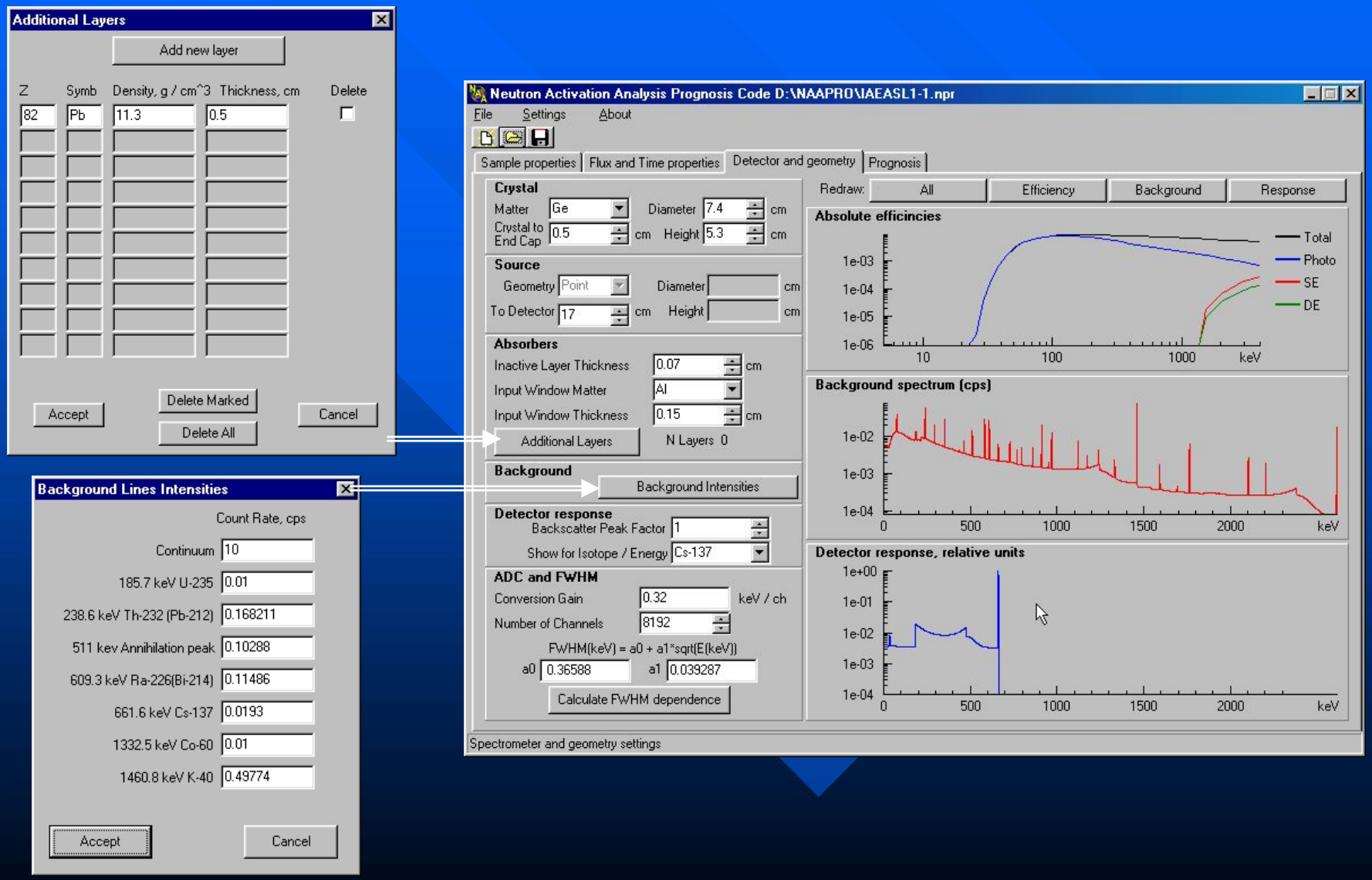




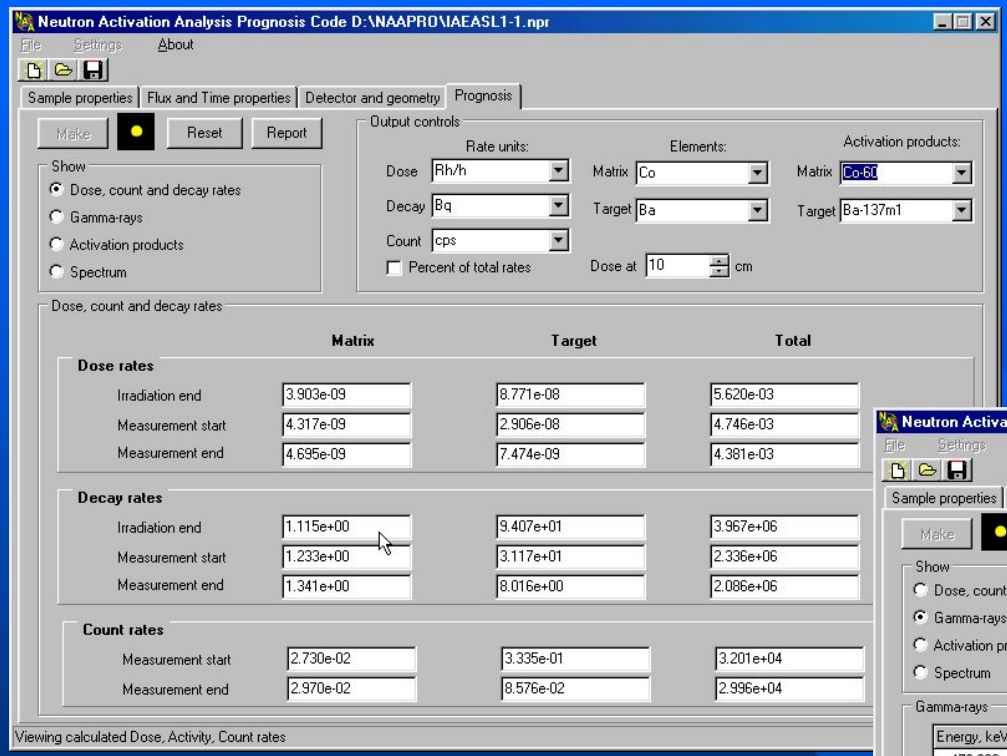
NAAPRO GUI: Flux and Time properties tab

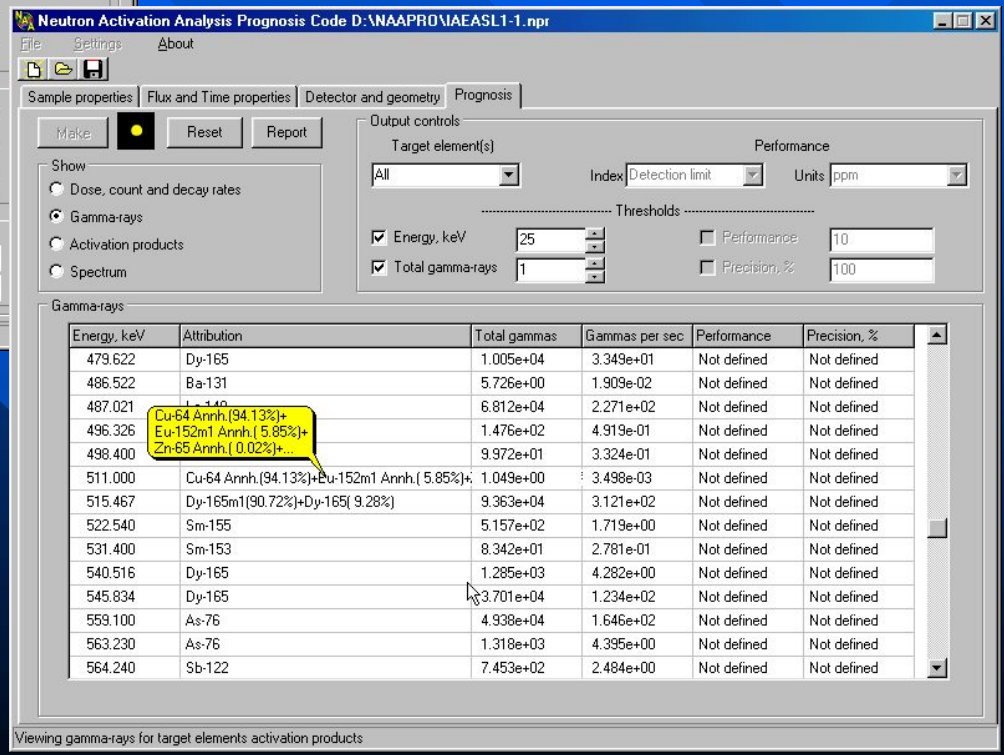


NAAPRO GUI: Detector and Geometry tab

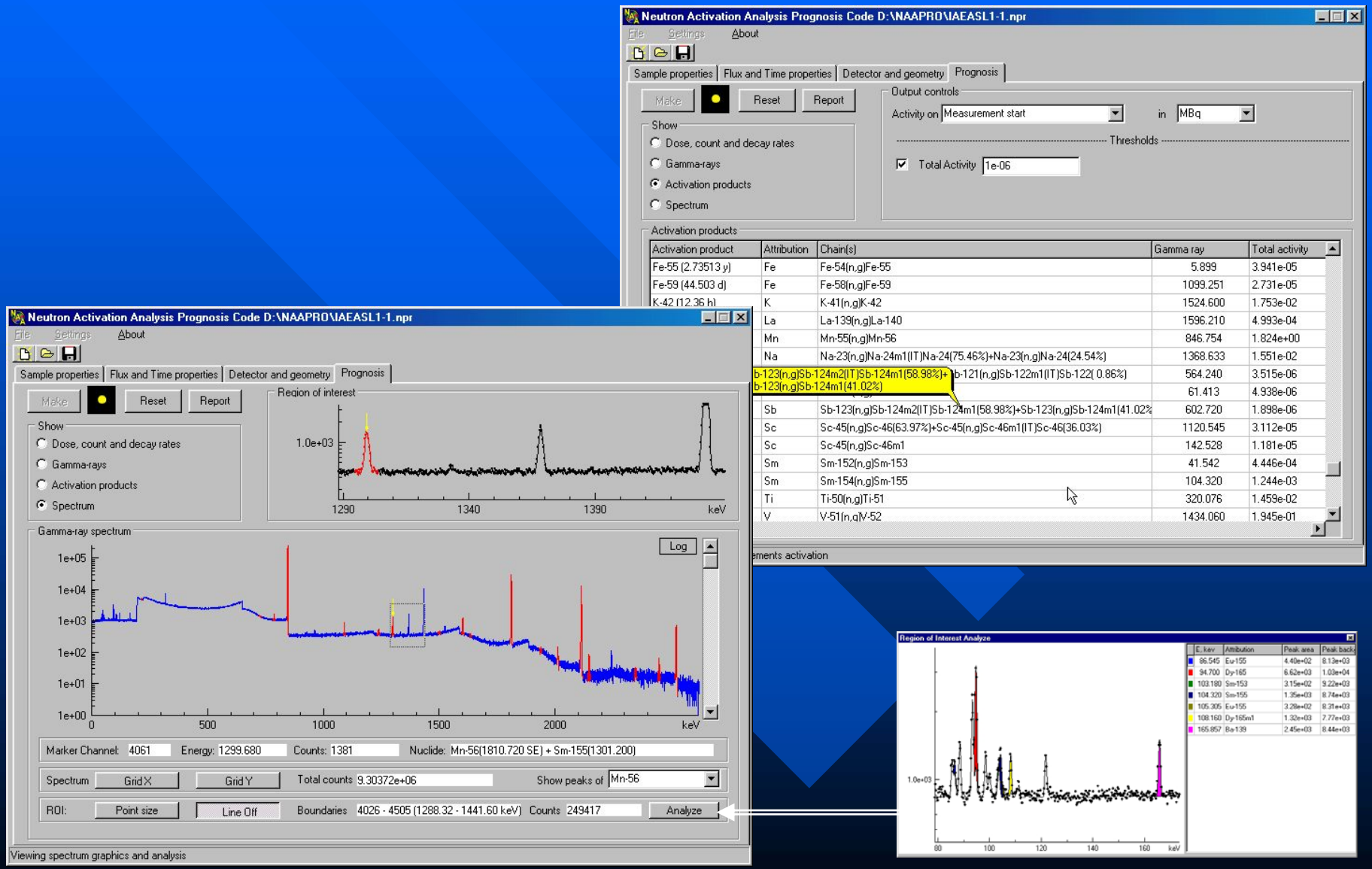


NAAPRO GUI: Prognosis tab





NAAPRO GUI: Prognosis tab



Thank you for your attention.